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CHARACTERIZATION OF VESICLE & MICROEMULSION  
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CHEMICAL ENGINEERING AND MATERIALS SCIENCE D F EVANS  
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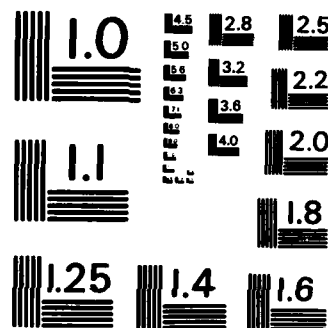
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  Strategies for controlling surfactant microstructure are described. An equilibrium between spontaneous vesicles and micelles is determined and interactions between charged surfaces using the surface forces apparatus are reported. A video enhanced contrast differential interference microscope was constructed.		

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CHARACTERIZATION OF VESICLE & MICROEMULSION MICROSTRUCTURES

Final Report

D. Fennell Evans

July 31, 1985

U.S. Army Research Office

*DAAG29-84-K-0152*

University of Minnesota

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## A. STATEMENT OF THE PROBLEM STUDIED:

This research is concerned with developing strategies for controlling the structure and stability of surfactant microstructures. These structures include micelles, vesicles, microtubules, bilayers and with added oil a range of bicontinuous materials and they play key roles in many biological and industrial processes. During the past year we have characterized an unusual micelle-vesicle equilibrium, demonstrating how the structures of bicontinuous microemulsions can be controlled by mixture of oil or surfactant and by the addition of cosurfactants. In addition we have assembled a video enhanced contrast differential interference microscope which permits direct visualization of surfactant microstructures.

## B. SUMMARY OF THE MOST IMPORTANT RESULTS:

### 1. Spontaneously Formed Vesicles

Dialkyldimethylammonium hydroxides form spontaneous, stable vesicles in dilute solution ( $10^{-3}$  M). This behavior is also observed when short chain carboxylate counterions are used. With increasing concentration the vesicles disappear and small spherical micelles with aggregation numbers of  $\sim 45$  form. This transformation, therefore, results in a decrease in aggregate size with increasing surfactant concentration and constitutes a striking departure from the generally accepted rules. Such behavior suggests that cationic surfactant aggregates in which hydroxide or carboxylate is the counterion possess unusual properties.

We have determined the equilibrium between micelles and vesicles as a function of surfactant concentration using a fluorescence probe-quencher technique. The results are shown in Fig. 1 for didodecyldimethylammonium hydroxide, acetate and butyrate. At  $10^{-3}$  M, the surfactant is entirely in the vesicle form; at  $10^{-1}$  M only micelles are present. The micellar aggregation numbers (within experimental error) were found to be constant across the entire concentration range.

Information on the interaction between vesicles which leads to the vesicle-micelle transformation was obtained from measurements on the surface forces apparatus. We were able to measure the force between the bilayers of dihexadecyldimethylammonium acetate as a function of distance in the range 1000A to contact. Such bilayers serve as a model for the interaction of vesicles upon approach to one another. The surfaces are highly charged with a potential of  $\sim 280$  mv. Addition of sodium acetate has only a small effect on the surface charge but  $1/K$  charges in a manner consistent with the predictions of the DLVO theory. There is no observable attractive minimum and the surfaces repel one another at all distances. This behavior is very different to that observed with the more commonly studied halides.

The observations summarized above suggest the following explanation. If vesicles of 300A diameter were concentrated so that the surfactant concentration were 0.1 M, they would be touching. Since the highly charged surfaces repel one



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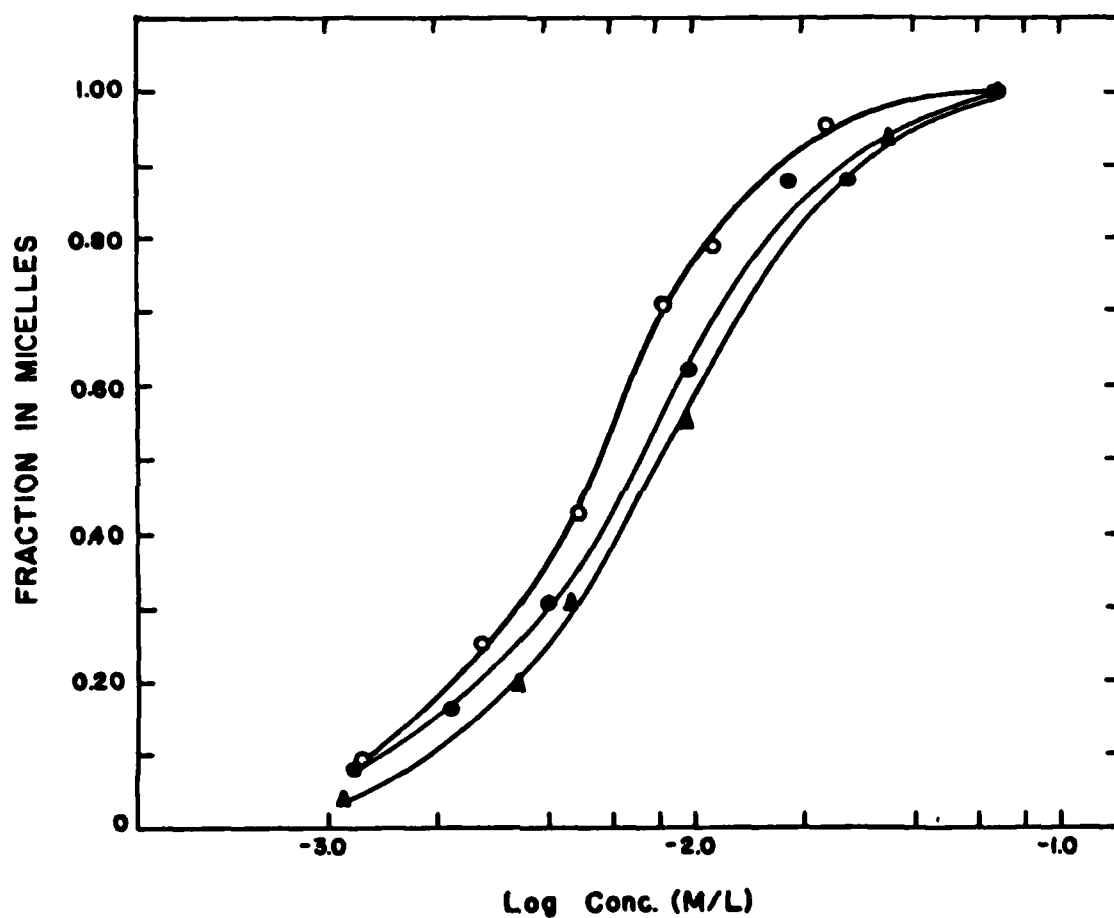


Figure 1. Fraction of didodecyldimethylammonium salt in micelles versus concentration: o, butyrate, ● acetate, Δ hydroxide. Vesicles predominate at low concentrations, micelles at high values.

another, the system must reorganize to a less bulky aggregate. One expects bilayers. However, with hydroxide or carboxylate as counterion, the very large intra-surfactant repulsive force within a given aggregate leads initially to the formation of micelles. At very high concentration of surfactant (~ 20 wt%) bilayers are finally formed. Experiments are underway to delineate the aggregation process of these unusual systems across the entire range of surfactant concentration.

Conductance experiments have been completed on the didodecyldimethylammonium carboxylates and show that there are no abrupt transformations or critical micelle concentration.

In addition to the studies described above, we have also determined cmc and aggregation numbers for the single chain dodecyltrimethylammonium hydroxide and carboxylates. The cmc and aggregation numbers are considerably smaller than those observed for the corresponding bromides.

A review article which discusses recent developments in colloid science has been accepted for publication the Journal of Physical Chemistry as a feature review article.

## 2. Three-Component Microemulsions

We have found that three-component microemulsions can be prepared using didodecyldimethylammonium bromide as the surfactant. This surfactant is insoluble in both oil and water and thus is located at the oil-water interface. This is an important design feature since it means that the oil-water interface area is set by the surfactant concentration. It is a simplifying factor in understanding the behavior of these systems and consequently offers many advantages over the more widely studied aerosol AOT three-component system.

These microemulsions show a number of unusual features: (i) there is considerable oil specificity; with hexane clear solutions are obtained upon addition of 4 volume % water (96% surfactant and oil) while for tetradecane 25% water is necessary. With the corresponding alkenes only ~ 1/2 as much water is required to form single-phase microemulsions. (ii) upon addition of more water the conductance decreases by many orders of magnitude, exhibits a percolation threshold (bicontinuous phases) and the microemulsion becomes oil continuous; still more water results in the formation of birefringent gels. The tetradecane system is an exception to this behavior, it remains water continuous at all compositions studied. (iii) with the minimum amount of water the viscosities of the microemulsions are high. Upon addition of water the viscosity decreases, goes through a minimum at the percolation threshold and subsequently increases. (iv) NMR diffusion coefficient established that these microemulsions are oil continuous at all computations.

The structure and properties of these microemulsions can be understood in terms of the curvature at the oil-water interface. This curvature is set by a delicate balance between head group repulsion and penetration of the surfactant chains by the oil which can be understood in terms of the surfactant number,  $v/\lambda a$ . During the past year we have investigated how mixtures of oil, mixtures of single and double-chain surfactants, addition of salts and co-surfactant can be used to control the curvature at the oil-water interface and thus set the structure of the microemulsion. In addition we have a study of the fluidity of surfactant interfaces using fluorescence anisotropy was undertaken.

A major review article summarizing the properties of three-component microemulsions was written and will be published in the Journal of Physical Chemistry as a feature review article.

### 3. Application of VECDIM to Characterization of Microemulsions

During the past year, we have assembled a Video Enhanced Contrast Differential Interference Microscope and built flow cells to study the effect of flow and chemically induced transformation on surfactant microstructure.

### C. LIST OF ALL PUBLICATIONS

"Rapid Characterization of Colloidal Systems by Video Enhanced Light Microscopy," B. Kachar, D. F. Evans, and B. W. Ninham, J. Colloid & Interf. Sci. **99**, 593 (1984).

A new microscopy technique, Video Enhanced Contrast Differential Interference Microscopy, is used to characterize colloidal systems by direct visualization on a T.V. screen. This method allows rapid characterization of colloidal surfactant aggregates and other macromolecules in the size range 500-10,000Å and offers a number of advantages over classical methods.

"Video Enhanced Contrast Differential Interference Microscopy, A New Tool for the Study of Association Colloids and Pre-biotic Assemblies," B. Kachar, D. F. Evans and B. W. Ninham, J. Colloid & Interface Sci. **100**, 287 (1984).

Progress in our understanding of molecular forces enables some rules to be formulated for design of surfactant systems. Competition between electrostatic and hydration head group forces, hydrocarbon chain interactions, associated oil penetrability, and interaggregate forces can be put to work to dictate prescribed curvature and other properties of association colloids. Such aggregates can be visualized directly and quickly by a new light microscopy technique. The power of this technique which complements QELS, neutron scattering, electron microscopy and other methods is illustrated by a study on several surfactant-water systems.



"Spontaneous Vesicles Formed from Hydroxide Surfactants — Evidence from Electron Microscopy," Y. Talmon, D. F. Evans, and B. W. Ninham, Science **221**, 1047 (1983).

Dialkyldimethylammonium hydroxide surfactants are highly soluble in water and form spontaneous stable vesicles. These vesicles can be grown to size with added acid, and appear to provide an ideal analogue membrane mimetic system for the study of fusion and ion transport. The existence of these phenomena is a consequence of strong hydration forces, not necessarily limited to the hydroxide ions. These forces can be put to work to design a variety of model systems. The observations are in direct contrast to the behavior exhibited by most double chained surfactants whether natural lipids or manufactured ionic compounds like didodecyldimethylammonium bromides which form insoluble liquid crystalline phases in water, and unstable vesicle suspensions on prolonged sonication.

"The Curious World of Hydroxide Surfactants: Spontaneous Vesicles and Anomalous Micelles," B. W. Ninham, D. F. Evans and G. J. Wei, J. Phys. Chem. **87**, 4538 (1983).

Double chained cationic surfactants typified by didodecyldimethylammonium bromide are insoluble in water, forming lamellar liquid crystal phases. They form vesicles only on prolonged sonication. If the halide ion is replaced by a hydroxide, the resulting surfactants are highly soluble and form spontaneously a clear solution which appears to comprise a mixture of small micelles and fairly monodisperse vesicles. The distribution of particle size changes with added base or with partial titration with acid (HBr, HCl, HF) which can sometimes yield vesicles with an initially unsymmetric distribution of anions. Evidence for these structures from quasi-elastic light scattering and viscosity measurements and an account of their extraordinary properties is presented.

"Unusual Behavior of Hydroxide Surfactants," S. Hashimoto, J. K. Thomas, D. F. Evans, S. Mukherjee and B. W. Ninham, J. Colloid & Interface Sci. **95**, 594 (1983).

Critical micelle concentrations, aggregation numbers, and degree of ion binding are reported for the single-chained surfactant tetradecyltrimethylammonium hydroxide in the presence of excess sodium hydroxide. Contrary to the usual structures with bromides or chlorides, where micelles undergo a rapid increase in size with added counterions, hydroxide micelles remain substantially unchanged up to high salt. The results indicate the existence of, and quantify, strong hydration forces associated with the hydroxide radical at a micellar surface which are also observed with corresponding double-chained vesicle-forming hydroxides.

"Spontaneous Vesicles" J. E. Brady, D. F. Evans, B. Kachar and B. W. Ninham, J. Amer. Chem. Soc. **106**, 4279 (1984).

Video Enhanced Differential Interference Contrast Microscopy (VEDICM) confirms spontaneous vesicle formation by a wide range of didodecyldimethylammonium salts. Didodecyldimethylammonium (DDA) fluoride, formate, acetate, propionate,

butyrate, glycinate, acrylate, tartarate (dianion), and oxalate (dianion) yield clear, isotropic, low to moderate viscosity solutions to at least 0.1 M. VEDICM reveals vesicle formation by the fluoride and carboxylate surfactants at  $10^{-5}$  to  $10^{-3}$  M surfactant concentration. Spontaneous vesicle formation by DDA glycinate, tartarate (-2), and oxalate (-2) is anticipated. DDA acrylate vesicles are polymerizable (via addition of  $H_2O_2$ ) to yield polymer stabilized vesicles. Sonication prior to polymerization does not appear to influence vesicle size. DDA trifluoroacetate, trichloroacetate, bromoacetate, benzoate, octanoate, oxalate (monoanion) and perfluorobutyrate yield cloudy solutions (bilayer dispersions) at  $10^{-5}$  to  $10^{-3}$  M. With the exceptions of DDA benzoate and DDA octanoate the vesicle forming surfactants are the DDA salts of weak acids ( $pK_a$  3.4-9.8).

"Three Component Ionic Microemulsions," L. R. Angel, D. F. Evans and B. W. Ninham, *J. Phys. Chem.*, 87, 538 (1983).

Necessary design features of microemulsions formed from cationic surfactant without any requirement for cosurfactant are illustrated by a study of microemulsions formed from didodecyldimethylammonium bromide in various oils. Ease of purification, preparation, and manipulation give this and related systems a considerable advantage over conventional systems in enhancing our understanding of microemulsions and emulsion behavior.

"Properties and Structure of Three-Component Ionic Microemulsions," S. J. Chen, D. F. Evans and B. W. Ninham, *J. Phys. Chem.* 88, 1631 (1984).

Partial phase diagrams, conductivity and viscosity of cationic microemulsions, formed from didodecyldimethylammonium bromide in various alkanes with water are reported. In the one-phase region the microemulsions are conducting at low water content, and exhibit a percolation type transition to a nonconducting state with increasing water. Parallel behavior is exhibited by the viscosity of these systems. At very high water content the one phase system becomes a rigid gel. The behavior is virtually the obverse of that usually observed for microemulsions which require cosurfactant, and shows that the distinction between microemulsions and emulsions is tenuous. A high and systematic degree of oil specificity is observed. The data are analyzed and are consistent with simple pictures of microemulsion structure based on mainly geometric considerations. Characteristic sizes ranging from 50Å up to 2000-5000Å can be achieved.

"Structure and Dynamics in Three-Component Microemulsions," F. D. Blum, S. Pickup, B. Ninham, S. J. Chen and D. F. Evans, *J. Phys. Chem.* 89, 711 (1985).

NMR self-diffusion coefficients are reported for three-component microemulsions formed from didodecyldimethylammonium bromide/water/alkane. For hexane through tetradecane the oil diffusion coefficients are approximately half as large as those of the bulk oils and independent of composition. Therefore the systems are oil continuous through the entire one-phase region. The diffusion coefficients for the surfactant are small and independent of composition. The water self-diffusion coefficients decrease with added water for hexane through

dodecane, and change in a manner consistent with the abrupt conducting-nonconducting transition, known to occur in this system. The microemulsions are bicontinuous in the conducting region, and disconnected water-in-oil droplets in the nonconducting region of the phase diagram. The phenomena reported clearly demonstrate the interplay between forces due to oil penetration and those due to head group interactions which control curvature and therefore microemulsion structure.

"Roles of Oils and Other Factors in Microemulsion Design," B. W. Ninham, S. J. Chen and D. F. Evans, J. Phys. Chem., **88**, 5855 (1984).

The role of oils in prescribing microemulsion formation and structure is illustrated by a comparison of three-component microemulsions formed from water, the double-chained surfactant didodecyldimethylammonium bromide, and alkanes or alkenes. The alkenes (1-hexene through 1-tetradecene) form water continuous microemulsions at a considerably lower water (~3% for hexene) than the corresponding alkanes.

"Liquid Crystals in a Fused Salt:  $\beta, \gamma$ -Distearoyl Phosphatidylcholine in Ethylammonium Nitrate," D. F. Evans, E. W. Kaler and W. J. Benton, J. Phys. Chem. **87**, 533 (1983).

The formation of liquid crystals of  $\beta, \gamma$ -distearoylphosphatidylcholine (DSPC) in N-ethylammonium nitrate, a low-melting fused salt, has been documented with polarizing microscopy and small-angle X-ray scattering. The  $L_{\beta'} \rightarrow P_{\beta'} \rightarrow L_{\alpha}$  transitions with increasing temperature are present in analogy with the behavior of DSPC in water. For a 1:1 (by weight) mixture the d spacing for the  $L_{\alpha}$  phase is 63Å and the surfactant head group area is 76Å<sup>2</sup>.

"Micelle Size in Ethylammonium Nitrate as Determined by Classical and Quasi-Elastic Light Scattering," D. F. Evans, A. Yamauchi, G. J. Wei and V. A. Bloomfield, J. Phys. Chem., **87**, 3537 (1983).

Aggregation of surfactants to form micelles in ethylammonium nitrate, a low melting fused salt, was investigated by classical and quasi-elastic light scattering. For tetradecylpyridinium bromide and hexadecylpyridinium bromide the following data were obtained: critical micelle concentrations  $8.0 \times 10^{-2}$  and  $2.0 \times 10^{-2}$  mol kg<sup>-1</sup>, micellar aggregation numbers 17 and 26, second virial coefficients  $1.64 \times 10^{-3}$  and  $1.30 \times 10^{-3}$  mol-cc g<sup>-2</sup> and hydrodynamic radii 14Å and 22Å respectively. The results are consistent with either a small classical spherical micelle containing only surfactant or a spherical mixed micelle containing surfactant and ethylammonium ions as a cosurfactant. The measured second virial coefficients are almost equal to those calculated for hard spheres and reflect highly screened electrostatic interactions in the totally ionized solvent.

"The Activity and Stability of Alkaline Phosphatase in Solutions of Water and the Fused Salt Ethylammonium Nitrate," D. K. Magnuson, J. W. Bodley and D. F. Evans, J. Phys. Chem. **13**, 583 (1984).

The fused salt ethylammonium nitrate has several properties which resemble those of the biologically important solvent water. In order to shed light on the role of solvent in determining protein structure we have examined the influence on ethylammonium nitrate on the activity and stability of the enzyme alkaline phosphatase. Significant, although reduced enzymatic activity was observed in ethylammonium nitrate solutions up to 60% (v/v) in water while the enzyme was stable to brief exposure to solutions as high as 80% (v/v) in the fused salt.

"Critical Micelle Concentrations for the Alkyltrimethylammonium Bromide in Water Over the Temperature Range 25 to 160°C," D. F. Evans, M. Allen, B. W. Ninham, and A. Fouda, J. Solution Chem., **13**, 87 (1984).

Critical micelle concentrations were determined by conductance measurements for the decyl, dodecyl, tetradecyl and hexadecyl trimethylammonium bromides in water at 25, 60, 95, 130 and 160°C. The results are discussed in terms of the equilibrium model and the nonlinear Poisson-Boltzmann model for micelle formation. The free energies of transferring a methylene group out of water and into the oil-like interior of the micelle are found to be -781 (25°C), -796 (60°C), -819 (95°C), -815 (130°C) and -787 (160°C) cal mol<sup>-1</sup>.

"Why Micelles Form in Water and Hydrazine: A Reexamination of the Origins of Hydrophobicity," M. Ramadan, D. F. Evans and R. Lumry, J. Phys. Chem. **87**, 4538 (1983).

Micelle formation, a typical "hydrophobic process" in water, has been studied in hydrazine. The standard free energies,  $\Delta G_0$ , for micellization are similar in the two solvents (-9.6 Kcal mol<sup>-1</sup> for water and -7.8 Kcal mol<sup>-1</sup> for hydrazine for sodium dodecylsulfate). The corresponding  $\Delta H_0$  values (-6.1 Kcal mol<sup>-1</sup> and -13.3 Kcal mol<sup>-1</sup>, respectively) and  $\Delta S_0$  values (11 gib mol<sup>-1</sup> and -18 gib mol<sup>-1</sup> respectively) are dramatically different. The differences between hydrazine and water are attributed to a large positive increment to both  $\Delta H_0$  (H<sub>2</sub>O) and  $\Delta S_0$  (H<sub>2</sub>O) accompanying the transfer of the surfactant hydrocarbon chain out of water. These increments nearly compensate each other and thus make only a small contribution to the free energy in the temperature range 25-45°C. This interpretation is bolstered by the almost identical free energy of transfer of a methylene group from water (-0.76 Kcal mol<sup>-1</sup>) and hydrazine (-0.71 Kcal mol<sup>-1</sup>) to the micelle. These results suggest that the lipophobic properties of water and hydrazine are very similar and that the unique structural properties of water do not play a dominate role. The critical micelle concentrations are reported for sodium octyl-, decyl- and dodecylsulfate and decyl- and dodecyltrimethylammonium bromide in hydrazine at 25, 35 and 45°C.

"Micelle Formation in Hydrazine-Water Mixtures," M. Ramadan, D. F. Evans, R. Lumry and S. Philison, J. Phys. Chem., accepted.

Critical micelle concentrations for sodium dodecylsulfate in hydrazine-water mixtures ( $X_{H_4N_2} = 0.20, 0.35, 0.50, 0.60, 0.75, \text{ and } 0.85$ ) at 25, 35 and 45°C are analyzed with the equilibrium model for micelle formation to give the thermodynamics of transfer of hydrocarbon chains from the solvent mixture to the oil-like interior of the micelle. In going from water to hydrazine,  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  vary almost linearly from -9.7 to -7.9 Kcal mol<sup>-1</sup>, -4.1 to -13 Kcal mol<sup>-1</sup> and 11 to -18 cal mol<sup>-1</sup> °C<sup>-1</sup> respectively. No indication of a dramatic change from the compensated enthalpy-entropy behavior characteristic of water to the polar liquid behavior characteristic of hydrazine is observed.

"Ion Binding and the Hydrophobic Effect," D. F. Evans and B. W. Ninham, J. Phys. Chem. 87, 5025 (1983).

Two apparently opposing interpretations of ionic surfactant aggregation are reconciled. Phenomenological constants ascribed to ion association at micellar surfaces are reinterpreted and shown to emerge naturally from a treatment of electrostatic head group interactions via an explicit approximate solution of the nonlinear Poisson-Boltzmann equation. Given critical micelle concentrations and aggregation numbers, the free energies, enthalpies and entropies of micellization can be calculated. Enthalpy-entropy compensation is studied with water as solvent, and earlier conclusions based on the phenomenological model confirmed. Hydrazine exhibits very different behavior. By removing one parameter from consideration, the theory shows considerable light on the nature and importance of chain interactions in determining micellar structure, and on the validity of fluid-interior models for micelles.

"Ion Binding and Dressed Micelles," D. F. Evans, D. J. Mitchell and B. W. Ninham, J. Phys. Chem. 88, 6344 (1985).

Analytic expressions for electrostatic curvature free energy derived from the nonlinear Poisson-Boltzmann equation are used to construct a theory of ionic micelles. The thermodynamics implicit in the ion-binding model is shown to emerge naturally without resort to Stern layers. Reconciliation of the two apparently opposed theories allows one to discriminate between real "ion binding" due to specific ion interactions, and that due to adsorption excesses.

"Video Enhanced Differential Interference Contrast Microscopy: Characterizing Colloidal Materials," D. F. Evans, J. Brady, B. Kachar and B. W. Ninham, J. Solution Chem. 14, 142 (1985).

Video enhanced differential interference contrast microscopy (VEDICM) permits an immediate, rapid characterization of association colloid aggregates and other colloidal aggregates by direct visualization on a television screen. Particles with sizes down to 500Å, their dynamics, fusion and slow flocculation can be directly pictured, recorded and analyzed in real time, freeze-frame, slow

motion or time lapse. It is precisely in the distance regime, 500-10,000Å, joining micellar chemistry to the field of biological structures, that classical techniques do have most difficulty. In this domain surfactant aggregates — vesicles, liposomes, microemulsions, microtubules — can exhibit an astonishing dynamic structural diversity and distribution of structures. These are highly sensitive to pH, salt, temperature, and surfactant concentration in ways which are partially understood at a theoretical level, but not formerly easily accessible.

In this paper, the VEDICM technique is described and its ability to follow the spontaneous growth and fusion of vesicles upon changes in chemical environment is presented.

"Thermodynamic Properties of Ethylammonium Nitrate-Water Mixtures," M. Allen, D. F. Evans and R. Lumry, J. Solution Chem. accepted.

Partial molar volumes at 15, 25 and 45°C and partial molar heat capacities and expansivities at 25°C for ethylammonium nitrate + water mixtures are reported. The results are compared with those for other aqueous cosolvents, particularly hydrazine and ammonium nitrate.

"Molecular Forces in the Self-Organization of Amphiphiles," D. F. Evans and B. W. Ninham, J. Phys. Chem., submitted.

Some good progress has been made in quantifying the mechanisms that drive the formation and set the structure of multimolecular aggregates like micelles, vesicles, bilayers and microemulsions. Parallel advances have been made in understanding the nature of molecular forces between surfaces at distances below 100Å. The interplay between these two areas provides new insights into the way that the physical chemistry of lipid self-assembly affects some biological processes.

"Counterion Specificity as the Determinant of Surfactant Aggregation," J. Brady, D. F. Evans, G. Warr, F. Freiser and B. W. Ninham, J. Phys. Chem., submitted.

Aggregation numbers and critical micelle concentrations are reported for dodecyltrimethylammonium salts with hydroxide and a range of carboxylates as counterion, with and without added salt. The micelles are unusual in that cmcs are higher, aggregation numbers and ion binding parameters much lower, than those for the corresponding halides. Aggregation numbers change slowly (~ 29 to 49) with added salt up to 1 molar. The micellar properties parallel those of corresponding double-chained dimethylammonium salts which exhibit normal behavior (insoluble, lamellar phase) for bromides, anomalous behavior (highly soluble, spontaneous vesicles) for carboxylates and hydroxide. With increasing surfactant concentration the vesicles revert to micelles. An explanation of these phenomena is given.

"Curvature as a Determinant of Microstructure and Microemulsions," S. J. Chen, D. F. Evans, B. W. Ninham, D. J. Mitchell, F. D. Blum and S. Pickup, J. Phys. Chem., submitted.

Curvature, set by a balance between repulsive head group forces opposed by hydrocarbon chain repulsion augmented by oil uptake in surfactant tails, is shown to be a major determinant of microemulsion structure. The case is argued through a comparison between physical properties of three-component systems and those systems in which these properties are altered by mixed oils, mixed surfactants, cosurfactants, temperature and oils which exhibit an extreme affinity for surfactant monolayers. The emerging picture is consistent with theories of self-assembly for surfactants in water, provided constraints imposed by geometry are recognized.

"Oil, Water and Surfactant: Properties and Conjectured Structure of Simple Microemulsions," D. F. Evans, D. J. Mitchell and B. W. Ninham, J. Phys. Chem., submitted.

Phase diagrams and physical properties of three-component ionic microemulsions are reviewed. It is argued that microstructure is set by curvature arising from a balance between repulsive head group forces and opposing forces due to oil uptake in surfactant hydrocarbon tails, together with an overriding constraint set by geometric packing. The picture which emerges is consistent with theories of surfactant-water aggregation, and can be generalized to include multicomponent systems.

#### D. LIST OF ALL PARTICIPATING SCIENTIFIC PERSONNEL

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